

NEXAFS of Nanocomposites Based on Dendrimer Polymer Networks

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Introduction: There is considerable interest in the development of nanocomposites based on dendrimers as host matrices. The intent is to take advantage of functionalized dendrimer interiors that can complex with an added constituent, resulting in nanocomposites for specific applications (as shown in Figure 1). Networks based upon radically layered copolymeric poly(amidoamine-organosilicon) (PAMAMOS) dendrimers modified with Cu^{2+} were characterized using near edge X-ray absorption fine structure (NEXAFS). Information on how the added constituent complexes with N and O incorporated within the starburst dendrimer was gained.

Methods and Materials: Crosslinked poly(amidoamine-organosilicon) (PAMAMOS) dendrimer films were prepared from dimethoxymethylsilyl-terminated PAMAMOS dendrimers, as reported elsewhere.¹ Using an *in-situ* preparation method, a methanol solution of desired salt (e.g., CuCl_2) was added directly into the solution of precursor PAMAMOS dendrimer in the same solvent, and crosslinking was performed. The samples had a continuous distribution of metal cations at a macroscopic level. NEXAFS was performed on the samples over energy ranges of 250 to 600 eV and 850 to 1050 eV under ultra-high vacuum using the U7A sample station. Observations of the N and O edges and the effects of added the constituents on these edges were made.

Results: NEXAFS partial electron yield (PEY) spectra for the base dendrimer and Cu^{2+} cation-containing equivalents were obtained and their difference was plotted after normalization to ascertain the effects and location of the added constituents (See Figure 2 for an example result). Greater negativity in the difference spectrum is indicative of stronger interaction between the electrophilic cations and the constituent moieties. The interaction of Cu^{2+} with the carbonyl O (and also N, not shown) was readily discernable.

Conclusions: Previous work using electron paramagnetic resonance (EPR)² left unclear which O type (carbonyl or ester) was key in the chelating of metallic cations in these dendrimer systems. The NEXAFS results clearly indicate that it is the carbonyl O along with the N moieties are responsible for the strong electrophilic interaction. The ester oxygens play no significant part in the binding of the cations to the network.

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References: 1. P. R. Dvornic et al., Ch. 16 in *Silicones and Silicone-Modified Materials*; ACS Symp. Ser. 729, 241-269, 2000. 2. M. F. Ottaviani et al., *J. Am. Chem. Soc.*, 116, 661, 1994.

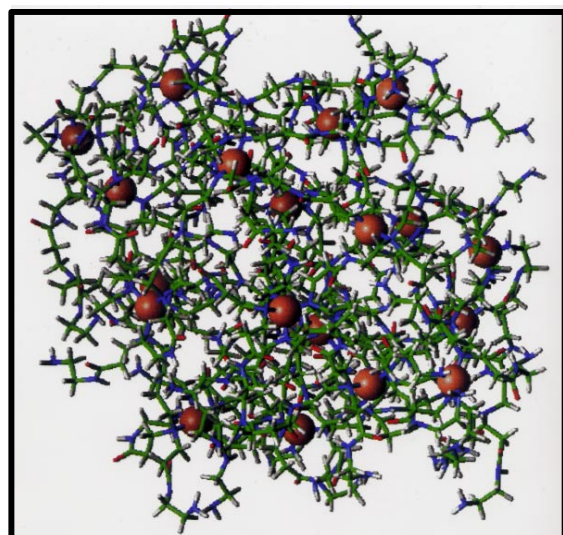


Figure 1. Molecular model of a generation 4 polyamidoamine (PAMAM) dendrimer with Cu tetracoordinated with the tertiary amines.

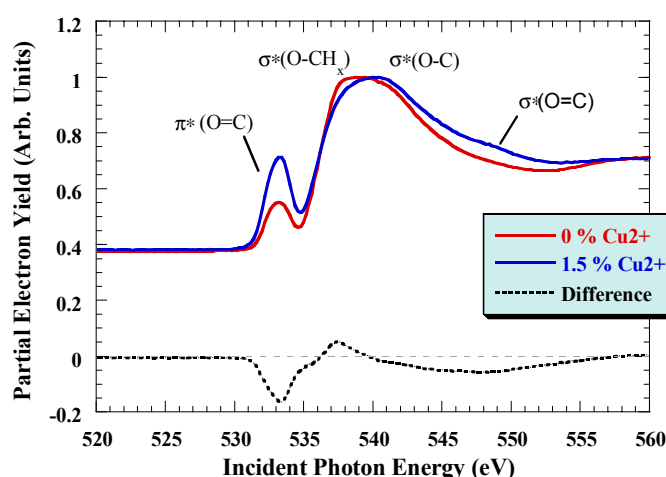


Figure 2. Normalized NEXAFS partial electron yield spectra for the O edge (at 55 deg. angle) for Cu^{2+} containing PAMAMOS[4,1]DMOMS dendrimer polymer networks and their difference. The 1s electron transitions are labeled.